

Surfactant Enhanced LNAPL Recovery and Attenuation

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Background

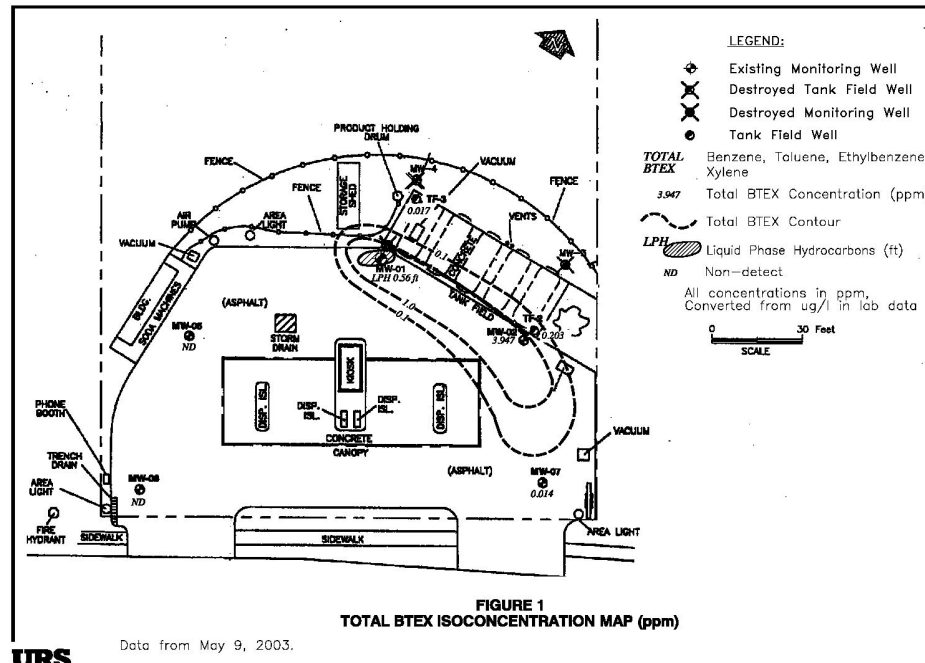
Many leaking underground storage tank cases, even those not considered to pose a threat to human health or the environment, remain open due to the periodic presence of residual light non-aqueous phase liquids (LNAPLs). Although the majority of the LNAPL has been removed at many of these sites, it is not unusual to find open environmental cases that exceed 10 years of age. The residual phase of the LNAPL continues to degrade ground water quality by partitioning into dissolved phase concentrations that can be in excess of regulatory criteria. Corporations have finite resources that they are able to allocate to the remediation of these types of sites. Although the individual budgets on these low-risk sites can be minimal, their collective impact on corporate environmental programs can be quite significant. In order to ensure that adequate funding is available for sites that truly pose a risk to human health and the environment and warrant active remediation, regulatory agencies and companies alike are evaluating alternative, non-traditional approaches and technologies for the cleanup of these low-risk sites. The expedited removal of residual LNAPL can help mitigate the source of the dissolved phase plume, minimize the risk to potential receptors, achieve regulatory compliance, and ultimately expedite case closure.

Approach

To accelerate cleanup and closure of these low-risk sites, two non-conventional remedial approaches have been combined: in-situ surfactant flushing and mobile multi-phase high-vacuum extraction. Surfactants are designed to change the interfacial tension between the water and NAPL bodies and desorb the residual LNAPLs entrained in the soil matrix by micro-emulsifying the organic particles, and forming a micelle. In the case of weathered LNAPLs, surfactants have been used to decrease the viscosity of the material, resulting in increased and more efficient recovery. Surfactants are also considered bioremediation enhancing and vapor suppression agents. The use of mobile multi-phase high-vacuum extraction allows the environmental engineer to focus remediation efforts at a targeted area of the site without incurring the cost and disruption associated with traditional permanent remediation approaches. Additionally, this method increases the effective radius of influence, while minimizing the volume of effluent recovered that requires treatment and/or disposal. This combined approach involves the in-situ application of a surfactant mixture, under pressure, into the site subsurface. The injection is followed by high-vacuum induced multi-phase recovery from an extraction well, via a mobile vacuum truck.

In addition to the physical removal of residual LNAPL and dissolved constituents during the flushing and extraction process, this study evaluated the solubilization and mobilization of the residual LNAPL and dissolved constituents following extraction. While there has been concern that the addition of a surfactant mixture may only result in the dilution and physical dispersion of any residual LNAPL and potentially increase the concentrations of the dissolved constituents, this study observed the successful mass phase transfer/removal following surfactant application/extraction and tracked the resulting attenuation of the dissolved constituents.

When surfactants are introduced into a water / NAPL system, they have two major results: 1) mobilization of free NAPL and 2) solubilization of residual NAPL. Of these two, mobilization is more rapid and has resulted in much of the negative views of surfactant use. In order to counteract the effects of mobilization and prevent unwanted migration, this study followed the surfactant injection with an extraction event to capture and remove the majority of the mobilized NAPL mass. Additionally, as shown with many other remediation technologies, more effective mass removal is achievable when a system is not allowed to achieve equilibrium. One example of this is the use of pulsed air sparging versus continuous air sparging. It was decided that the combined use of an injection and extraction event in close temporal proximity could help achieve this desired "push-pull" type of disequilibrium.



Site Background

The site selected for this test is an operational retail gasoline service station. The site is located in the southern portion of Maryland, within the Coastal Plain. The lithology of the site is characterized by interbedded alluvial sands, silts, clays and gravels. Ground water at the site is found at a depth of approximately 15-feet below ground surface. Ground water at the site generally flows to the southwest at an approximate gradient of 0.0003 feet/foot. Figure 1 depicts a map that shows the general features of the site and the location of the injection / extraction and monitoring wells as well as total benzene, toluene, ethylbenzene, and xylenes (BTEX) concentrations detected in the monitoring wells prior to applying the surfactant.

There has been an open environmental case at the site since 1984, due in part to the intermittent presence of LNAPL in several of the ground water monitoring wells at the site. Although the case has been open for over two decades, active remediation was not undertaken due to the limited areal distribution of LNAPL and high dissolved BTEX in the ground water at the site. Additionally, since only the surficial, water-table "aquifer" was impacted and the site is not located in an area with potable wells, active remediation was not deemed necessary to protect human health and the environment. The case could not be closed previously due to the limited presence of LNAPL in one of the monitoring wells (Maryland regulations prohibit the closure of cases with LNAPL present and require the removal of LNAPL to the maximum extent practical – a sheen). Environmental activities at the site were limited to quarterly ground water monitoring and the use of passive bailers for LNAPL recovery.

Historically, a dissolved BTEX plume has extended from the area of the underground storage tank (UST) tank field to the area of well MW-7. Well MW-1 has historically contained several inches of LNAPL, while well MW-2 has contained periodic traces of LNAPL. The maximum LNAPL thickness reported historically in well MW-1 was approximately 1.40 feet. However, at the beginning of the pilot test, MW-1 contained approximately 0.56 foot of LNAPL.

Surfactant Injection / Extraction Event #1

On October 6, 2003, all wells at the subject site were gauged. Monitoring well MW-1 was found to contain 0.56 foot of LNAPL and MW-2 was found to contain 0.01 foot of LNAPL. Following well gauging and preparation of necessary materials, 150 gallons of 4% solution proprietary-blend non-ionic surfactant (EC-165, EnviroClean, LLC) was injected into well MW-1. Approximately 100 gallons of 3% solution surfactant was

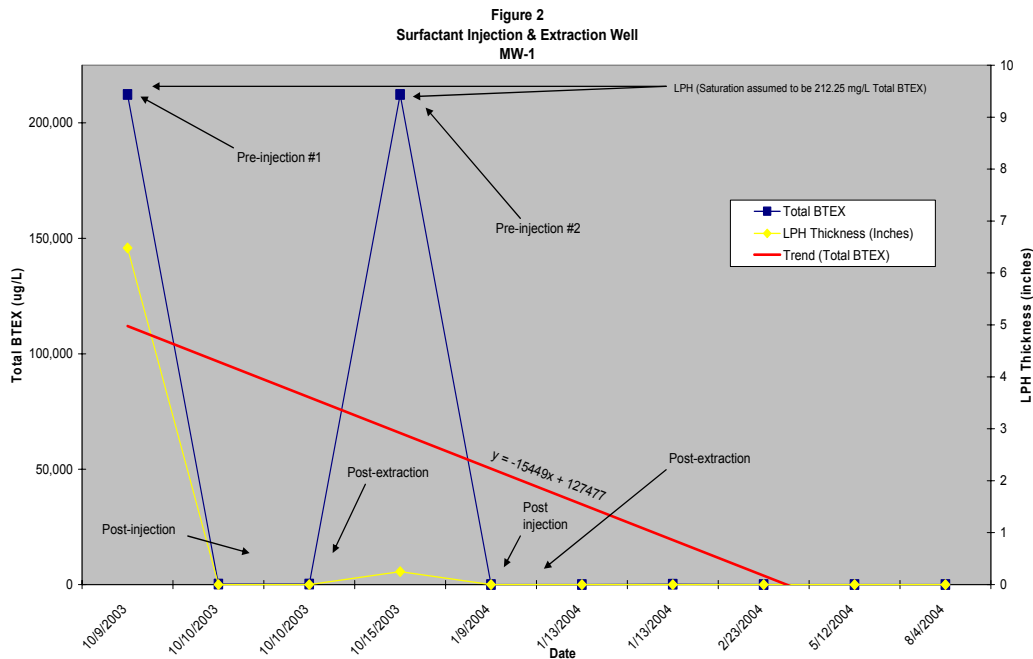
injected into well MW-2. The surfactant mixture was injected through a down-well surge block at a flow rate of approximately 5 gallons per minute (gpm) and a pressure of approximately 15 pounds per square inch (psi). It was estimated that the surfactant mixture achieved a radius of influence of approximately 10 feet around the injection wells. Based on literature research of surfactants, the surfactants were left in the ground for a period of approximately 72 hours prior to extraction.

On October 9, 2003, all wells at the subject site were gauged. MW-1 and MW-2 were not found to contain any LNAPL. Following well gauging, a vacuum truck equipped with a down-well drop-tube and well seal was utilized to evacuate the liquid in the two injection wells, under vacuum. Approximately 500 gallons of water, LNAPL, and emulsion was removed from well MW-1 and approximately 300 gallons of water and emulsion was removed from well MW-2.

Following completion of the first surfactant injection and extraction event, the monitoring wells at the site were gauged several times. Approximately 0.02 foot of LNAPL was detected in MW-1 one week subsequent to the completion of the extraction event, and LNAPL did not return to MW-2. Due to the presence of residual LNAPL in MW-1, it was decided that one additional surfactant application would be conducted.

Ground Water Monitoring Results Subsequent to Event #1

Subsequent to the first surfactant injection / extraction event, but prior to the second event, a round of ground water samples was collected from all of the monitoring wells at the site. A >99.99% reduction in total BTEX concentrations was observed in injection / extraction well MW-1 and a 97% reduction in total BTEX concentrations was observed in injection / extraction well MW-2. BTEX concentrations in downgradient wells MW-5 and MW-6 remained non-detect during this sampling period. However monitoring well MW-5 did exhibit a slight increase in methyl tertiary butyl ether (MTBE) concentrations (64 parts per billion [ppb] to 285 ppb). A slight increase in dissolved BTEX concentration was observed in Well MW-7 (14 ppb to 68 ppb) subsequent to the first injection / extraction event. The ground water monitoring results from MW-1 are included in Figure 2. The ground water monitoring results from MW-2 are included in Figure 3.



Surfactant Injection / Extraction Event #2

On January 9, 2004, all wells at the subject site were gauged. MW-1 and MW-2 were not found to contain any LNAPL. However, due to the presence of relatively high levels of dissolved BTEX in the vicinity of the two

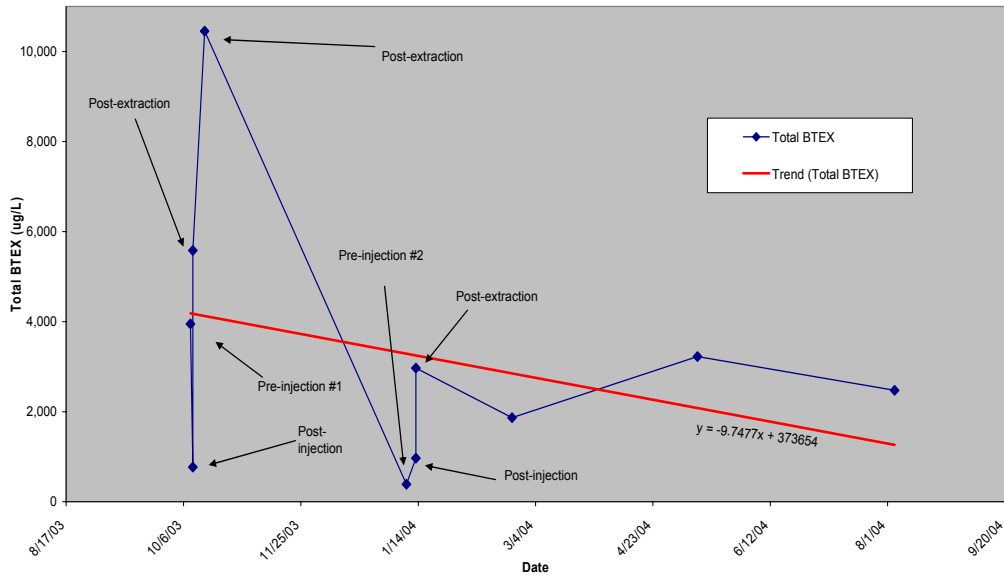
injection / extraction wells, a second surfactant injection and extraction event was completed. Following well gauging and preparation of necessary materials, 200 gallons of 5% solution proprietary-blend non-ionic surfactant (EC-165, EnviroClean, LLC) was injected into well MW-1. Approximately 100 gallons of 5% solution surfactant was injected into well MW-2. The surfactant mixture was injected through a down-well surge block at a flow rate of approximately 5 gpm and a pressure of approximately 15 psi. The surfactants were left in the ground for a period of approximately 96 hours prior to extraction during this injection event.

On January 13, 2004, all wells at the subject site were gauged. MW-1 and MW-2 were not found to contain any LNAPL. Following well gauging, a vacuum truck equipped with a down-well drop-tube and well seal was utilized to evacuate the liquid in the two injection wells, under vacuum. Approximately 390 gallons of water and LNAPL emulsion was removed from well MW-1 and approximately 625 gallons of water and LNAPL emulsion was removed from well MW-2.

Ground Water Monitoring Results Subsequent to Event #2

Subsequent to the second surfactant injection / extraction event, a round of samples was collected from all of the ground water monitoring wells at the site. Approximately an additional 60% reduction in total BTEX concentrations was observed in injection / extraction well MW-1, for a net reduction of >99.99% over pre-test concentrations, and a net 40% reduction in overall total BTEX concentrations was observed in injection / extraction well MW-2. BTEX concentrations in downgradient monitoring well MW-5 went from non-detect levels of benzene to a detectable concentration of 1 ppb. MTBE concentrations in monitoring well MW-5 increased from 285 ppb to 555 ppb. Downgradient monitoring well MW-6 remained non-detect for BTEX and MTBE. BTEX concentrations in monitoring well MW-7 slightly increased from 68 ppb to 80 ppb. The ground water monitoring results from MW-1 are included in Figure 2. The ground water monitoring results from MW-2 are included in Figure 3.

Figure 3
Surfactant Injection & Extraction Well
MW-2

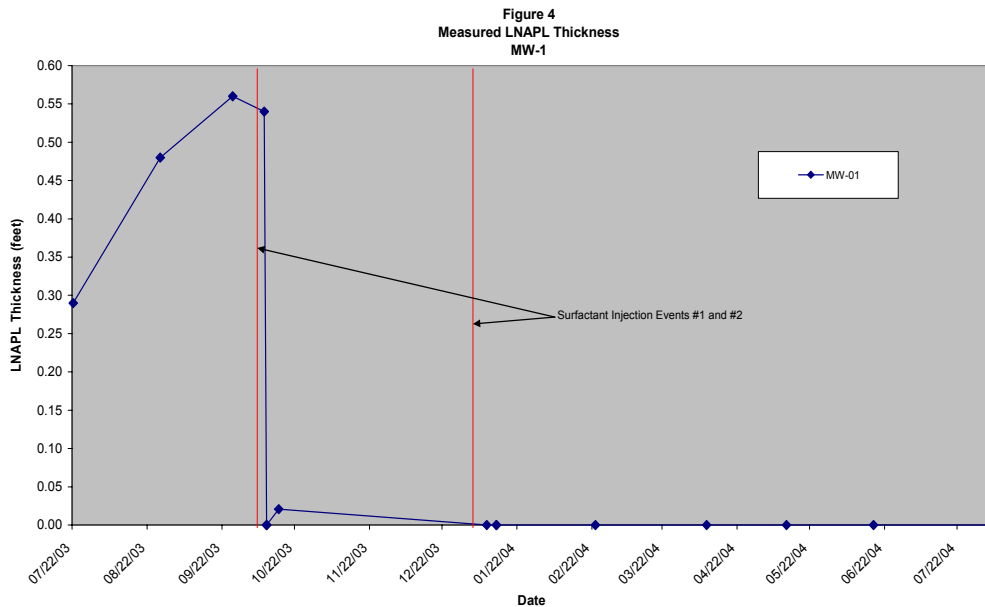


Ground Water Monitoring Results in Surfactant Injection / Extraction Wells

The study found that LNAPL was not observed in any of the test sites following the two surfactant injection and extraction events. The LNAPL reduction observed in MW-1 was significant. Prior to the initiation of the test, MW-1 contained 0.56 foot of LNAPL. Subsequent to the completion of the test, MW-1 was found to not contain measurable LNAPL. LNAPL monitoring results are depicted in Figure 4. Also, the study found that

dissolved BTEX concentrations in the injection / extraction wells was reduced by 99.99% and 18% in wells MW-1 and MW-2, respectively, following the two surfactant injection and extraction events.

As discussed previously, the two main mechanisms associated with the use of surfactants in a water / oil system are mobilization and solubilization. Both of these mechanisms were observed during the study. First, the majority of the LNAPL mass in the site subsurface was mobilized following the injection of the surfactant solution. Within several days of the injections, Winsor Type III reactions were observed in MW-1. The Winsor Type III reaction is characterized by the presence of three distinct phases: an aqueous or dissolved phase, a micro-emulsion phase, and a NAPL phase. During the vacuum extraction event performed on October 9, 2003, this multi-phase phenomenon was observed. Fluids recovered from the vicinity of MW-1 included hydrocarbon-impacted ground water, micro-emulsion globules, and LNAPL. The amount of fluid recovered from well MW-1 was approximately 500 gallons. It was estimated that approximately 25% of this fluid consisted of NAPL and micro-emulsion, with the remainder of the mixture being comprised of impacted ground water and surfactant solution. Within a relatively short period of time (several days to weeks) following the initial injection / extraction event, dissolved BTEX concentrations in well MW-2 increased significantly. During this same period of time, residual LNAPL in the vicinity of MW-1 continued to be mobilized by the residual surfactant. The occurrence of the residual surfactant was confirmed during subsequent monitoring events, visually by the presence of a tracer dye that was included in the surfactant formulation. Following the initial extraction event on MW-1, no LNAPL was detected. However, within one week after the extraction event, the LNAPL thickness in MW-1 had returned to 0.02 foot. Solubilization of the LNAPL mass present in the site subsurface was observed during this study; however, mobilization appeared to be the predominant mechanism, followed by solubilization. As shown in Figure 3, there was a marked increase in dissolved BTEX concentrations immediately following the initial surfactant injection. As shown in this figure, however, the relatively high dissolved BTEX concentrations appeared to quickly attenuate. It is believed that the surfactant released the NAPL mass from the relatively unavailable residual phase into the extremely bioavailable dissolved or aqueous phase, where it can be readily broken down by resident microbe populations.



Ground Water Monitoring Results in Downgradient Wells

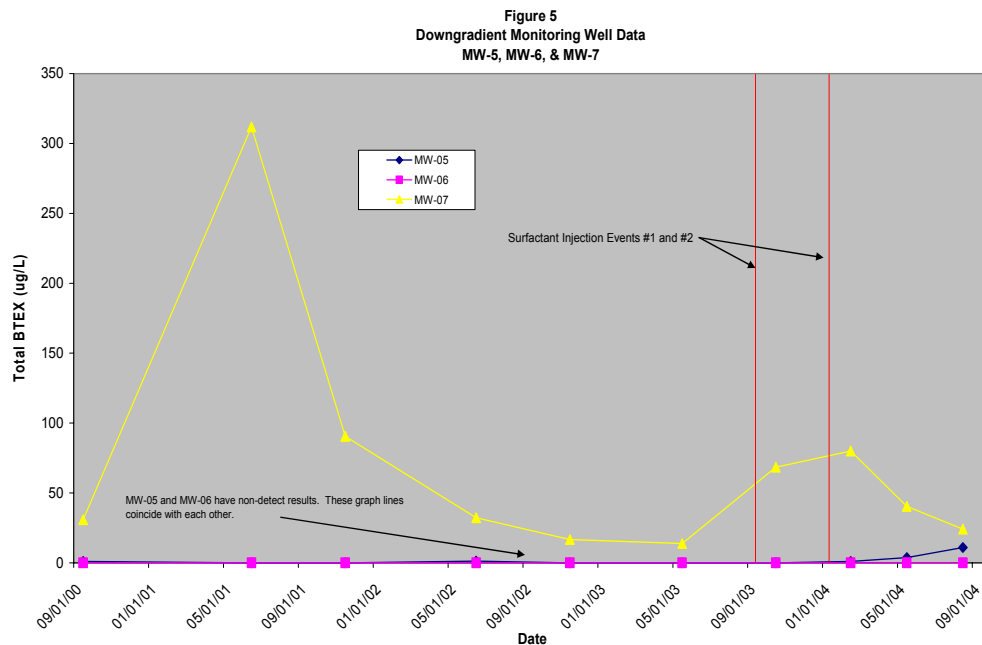
There is concern that the surfactant treatments can be simply diluting, displacing, or dispersing the LNAPL mass and result in creating a more dissolved fraction. In order to evaluate this potential concern, close attention was given to the two ground water monitoring wells located hydraulically downgradient from the surfactant injection / extraction wells, MW-1 and MW-2. Figure 5 depicts the results of ground water samples collected from downgradient wells MW-5 and MW-6, as well as the side gradient well MW-7. Given the historical

direction of ground water flow at the site and the spatial proximity to the source and treatment area, special consideration was given to well MW-5.

As to the concept of dilution, during the initial surfactant injection event, approximately 250 gallons of surfactant solution were introduced into the subsurface in the areas of MW-1 and MW-2. The volume of non-native fluid introduced into the system is <0.5% of the total volume of the water contained in the area between MW-1 and MW-2. It is highly unlikely that this extremely small volume of water, relative to the water volume of the test area, resulted in the initial concentration reductions of 97% to >99% observed during the first phase of the test.

With regard to the role displacement and dispersion play on this site, the data collected from the downgradient monitoring wells may support limited contribution due to these mechanisms. Immediately following the first and second surfactant injection / extraction events, the dissolved petroleum concentrations in MW-5 increased. Benzene concentrations went from non-detect to 9 ppb. BTEX concentrations went from non-detect to 11 ppb. MTBE concentration went from 64 to 1,960 ppb. If a correlation does exist (there are no contributions from current operations at the service station), the decrease in mass observed in the areas of MW-1 and MW-2 would likely result in significantly higher dissolved petroleum concentrations than those observed in MW-5. It should also be noted that within 3-4 days of injection, the surfactant solution was extracted. In fact, 3-4 times the initial injection volume was recovered and removed by the vacuum extraction unit.

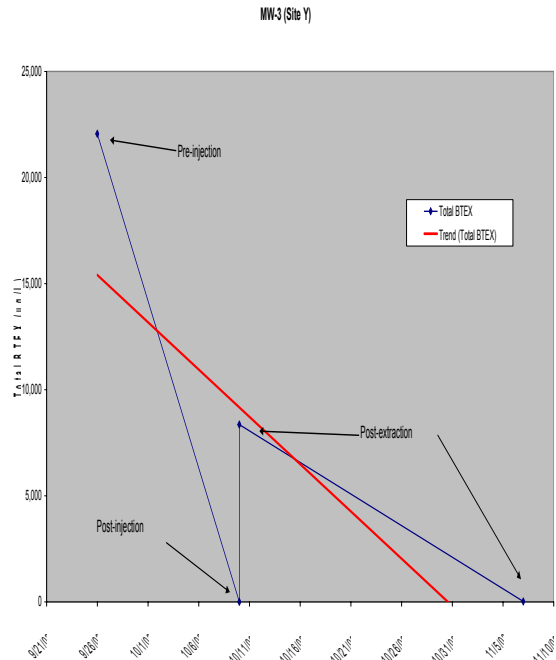
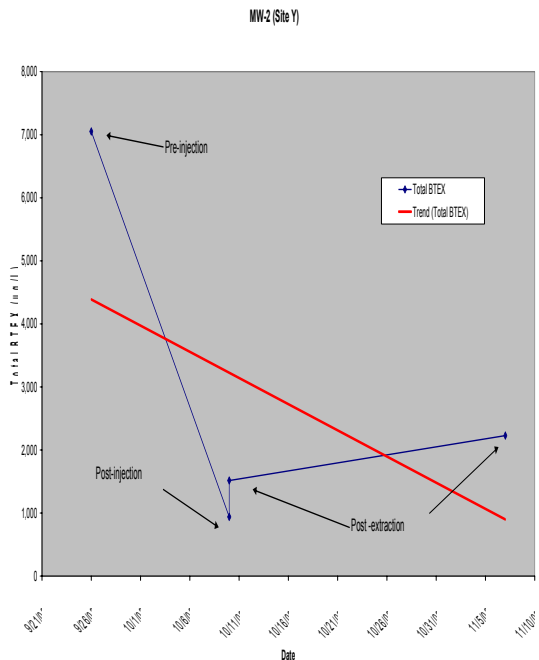
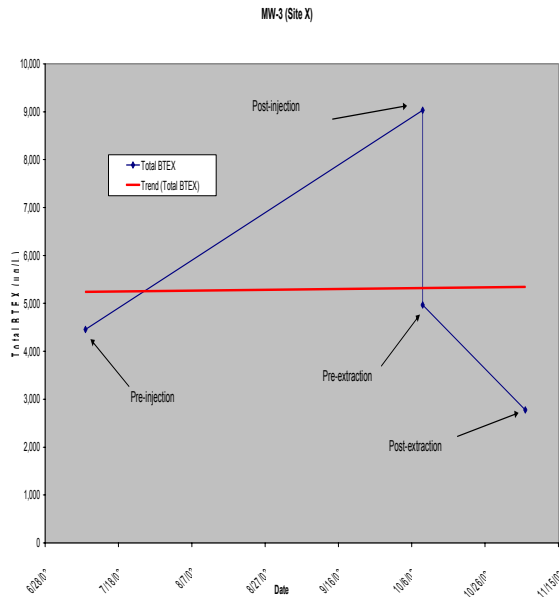
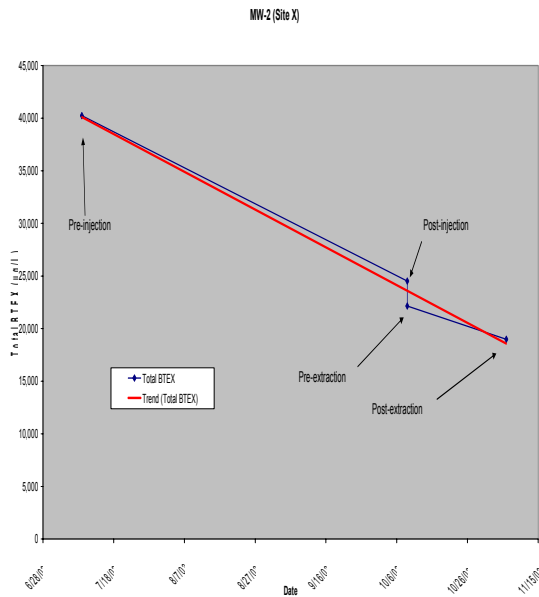
In the absence of dilution, dispersion, or displacement as the mechanisms for the attenuation observed at the site, the ideas of bioavailability and biodegradation are given more weight. Although no microbial samples were collected as part of this study and biodegradation was not directly studied, anecdotal evidence supports the occurrence of enhanced biodegradation subsequent to the injection / extraction events. It is believed that the significant attenuation rates observed in wells MW-1 and MW-2, subsequent to the injection / extraction events is due to the increased bioavailability of the contaminant mass as a by-product of increased solubilization.



Results from Additional Test Sites

The results of this study were promising and the technology was employed at several other sites throughout Maryland. Results observed at this site were consistent with the results observed at the other sites. The following graphs show the results from two other surfactant injection / extraction sites. Although the results are not quite as remarkable as those from the study site, the results are consistent with the observations at the study

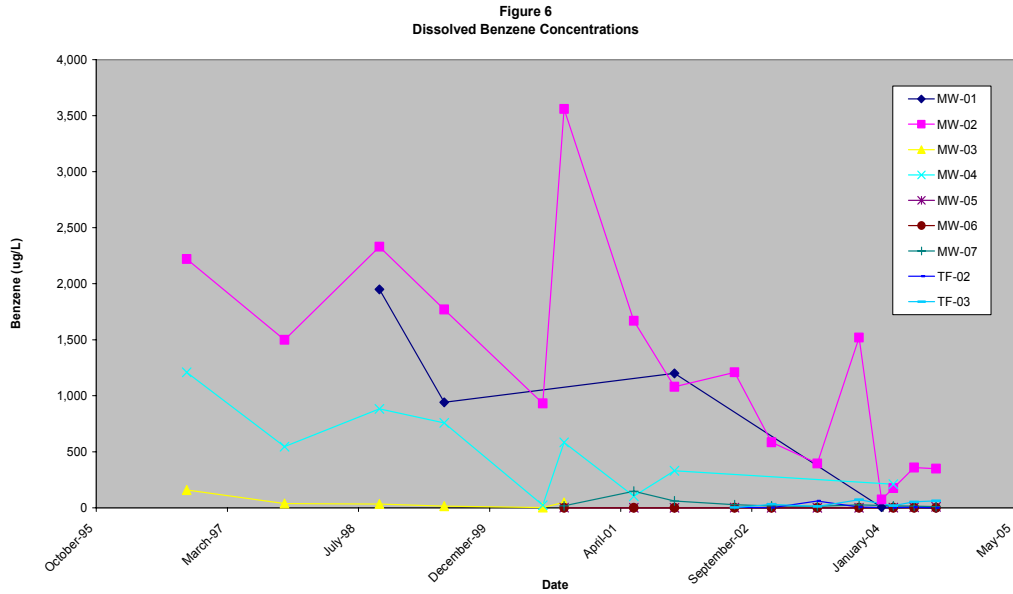
site. It should be noted that the wells presented below contained only relatively high levels of dissolved BTEX and did not contain LNAPL as the study site did.



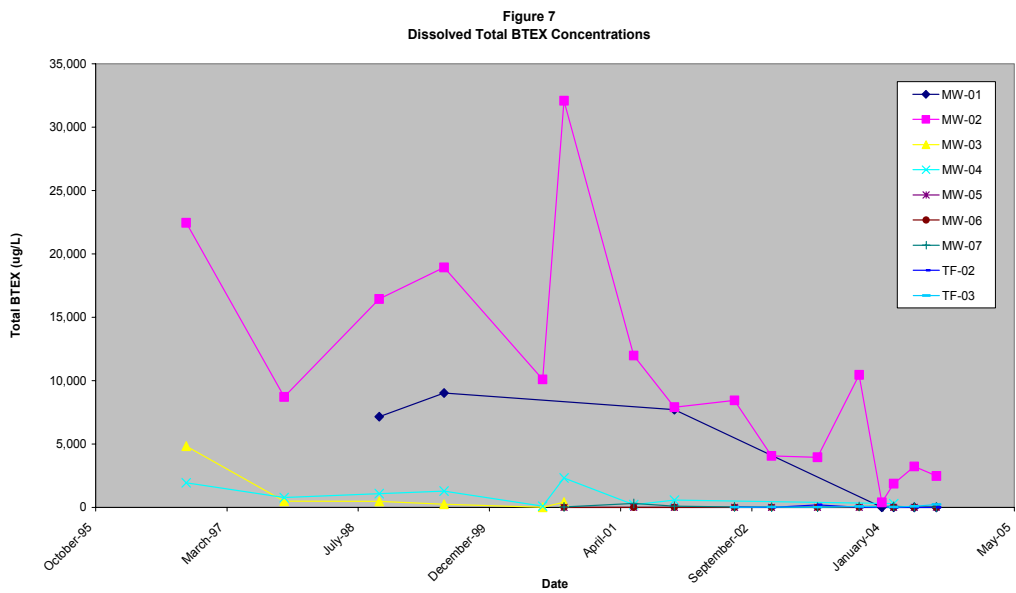
Conclusions and Path Forward

The goal of this study was to determine if surfactant injection / extraction could be a viable remediation option for low-risk petroleum sites that did not warrant full-scale active remediation efforts. Many sites and environmental cases exist that do not pose a significant risk to human health or the environment, but must remain open due to the continuous or intermittent presence of small amounts of LNAPL. In the State of Maryland, a site that has been shown to not pose a significant risk can be closed once LNAPL is removed and a declining contaminant mass and/or concentration trend is shown. Ultimately, the surfactant injection /

extraction events employed at the subject site were able to remove all the persistent measurable LNAPL from the site monitoring wells. The closure request for this site has been submitted and approved pending a final compliance inspection at the site (it is an operational retail gas station) by the Maryland Department of the Environment regulator.



Figures 6 and 7 depict the dissolved benzene and Total BTEX concentrations observed at the site over time. Based on this data, and the resulting case closure, this form of remedial application appears to be successful. The client was able to achieve case closure in a period of a little more than one year, at a cost of approximately \$25,000 (including monitoring costs). Operations at the site were minimally disrupted by the surfactant injection / extraction project, as it can be deployed as a mobile technology.



Future studies will focus on the biodegradation of the dissolved phase of the contamination. This study demonstrated the successful physical removal processes of LNAPL from affected areas. Additional study is required to evaluate the processes of bioavailability and potential limiting factors that may affect

biodegradation. If the surfactant injection / extraction technology is applied to a site, it is important to understand the biochemical parameters at the site that may limit the rate of removal so that if an increase in dissolved phase concentrations is observed in downgradient wells, measures can be put in place to address these potential concerns. These biochemical parameters may include dissolved oxygen concentration, CO₂, ORP, pH, sulfate, sulfide, nitrate, nitrite, iron, alkalinity, BOD, COD, methane and bacterial plate counts. It is recommended that the biochemical and hydrogeologic parameters be understood at sites where there may be risk to potential downgradient receptors prior to incorporating this technology.

Biographical Sketches of the Authors:

Robert J. Tworkowski is a Professional Geologist with over 20 years of experience in the field of environmental site assessment and remediation. Mr. Tworkowski works for URS Corporation, and manages a Remediation Services Group that provides services primarily to the petroleum sector. Mr. Tworkowski has a BS degree in Geology from Rutgers University.

Jason L. Baer is a Registered Environmental Manager with over 10 years of experience in the field of environmental site assessment and remediation. Mr. Baer, formerly with URS Corporation, currently works for the State of Maryland, Maryland Environmental Service as a Project Manager, specializing in the remediation of petroleum- and solvent-impacted sites. Mr. Baer has a BA degree in Liberal Arts from St. Mary's College of Maryland and an MS in Environmental Management from the University of Maryland.